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**Fabrication of high-performance polymer bulk-heterojunction  
solar cells by the interfacial modifications III.**

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## I. Abstract

This research investigates three primary tasks for fabrication of high performance polymer-bulk-heterojunction solar cells. i) The analysis of the very unique poly(ethylene-oxide) functionalized polymer:Al complex electrode through an co-evaporation process for polymer light-emitting diodes (PLEDs) and bulk-heterojunction (BHJ) solar cells. ii) Interfacial modification at organic/metal junction by self-assembly, well-organized tetraoctylammonium bromide (TOAB) salts for organic electronics devices iii) The studies of magneto responses for P3HT photovoltaic cells under the post-annealing conditions.

## II. Progress summaries

### **(i) The development of the very unique poly(ethylene-oxide) functionalized polymer:Al complex electrode through an co-evaporation process for polymer BHJ solar cells**

Our research had demonstrated a non-conventional cathode design to fabricate efficient PLEDs and polymer BHJ solar cells. By changing the compositions of two components, co-evaporation of PEGDE polymer with Al metal in vacuum at variable ratios, one can fine tune the electron-injection capability of cathode to balance the injected charge carriers (electrons and holes) and achieve the optimal device performance. The cathode buffer reported in this research takes advantage of the instant chemical reaction between the ethylene oxide functional groups with atomic Al in vacuum through a unique thermal co-evaporation process. Several tasks to put together different polymers with various metals for the preparations of cathode buffers had been conduct, but the combinations of organic molecules carrying the ethylene oxide functional group usually works best with Al as the complex cathode for PLED and BHJ solar cells, having the highest luminous efficiency as well as the power conversion efficiency. The PLEDs and polymer BHJ solar cells applying PEGDE:Al/Al cathodes also present the superior performance than that of devices with low work function metal cathodes. This work disclosed the origins of the organic molecules/Al junction and further utilize the interfacial reactions for the fabrications of efficient PLEDs. The salt-free, neutral interfacial layer can be easily integrated into the studies of other organic electronic devices, currently in progress.

### **(ii) Interfacial modification at organic/metal junction by self-assembly,**

## **well-organized tetraoctylammonium bromide (TOAB) salts for organic electronics devices**

For organic electronics devices, the usage of the low work function metals (such as Ca or Ba) as a cathode to achieve high efficiency are the problems for the long term stability and the practical applications. To circumvent the problems of stability, it is desirable to use high work function metals (such as Al, Ag, and Au). Among many approaches by inserting a thin layer between Al (Ag or Au) and the light-emitting polymer, the conjugated polyelectrolyte or surfactant is the most efficacious. However, the complicated structure and the purification problem render them unfit for a practical application. Herein, we first disclose that the formation of layered structure of tetraoctylammonium bromide (TOAB) on green-emissive poly(9,9-dioctylfluorene) derivative (G-PF) gives extra-high electroluminescence efficiency. The device with ITO / poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) / G-PF / TOAB / Al gives 15.4 cd/A for the maximum electroluminescence efficiency and 56315 cd/m<sup>2</sup> for the highest luminance at 8V. The unique contribution of our finding is that our results can be indisputably repeated and widely applied to other organic electronics devices.

### **(ii) The studies of magneto responses for P3HT photovoltaic cells under the post-annealing conditions**

The variations of magneto conductance (MC) responses in the post-annealed regioregular poly(3-hexylthiophene) (P3HT)-based polymer photovoltaic devices was studies in our research. The short-circuit current ( $I_{sc}$ , photocurrent measured at 0V bias voltage) for P3HT-based photovoltaic of Al electrode (P3HT/Al-device) without the post-annealing process has a positive MC response in  $I_{sc}$  of ~5.0% at B=1000mT. upon post-annealed at 150°C for few minutes (5~90 minutes), the maximal magnitudes of MC responses were decreased with the post annealing time. The decreases in MC responses are correlated with the elevated open-circuit voltage for P3HT/Al-devices by thermal annealing process. The increased built-in electrical filed presumably facilitates dissociation of photo-excited states, but reduces the influence from the applied magnetic field and declines the MC response. A negative MC component, resulting in the gradually decreased MC responses in the high magnetic field (>300 mT), were also observed in  $I_{sc}$  the post-annealed P3HT/Al-devices at 150°C for 90 minutes due to the reduced triplet exciton-charge reactions.

### **III. Summary of Accomplishments**

- 1. "Magneto conductance responses in post-annealed polymer photovoltaics"** submitted. **(AOARD-10-4054)** (**Joint research work with Prof. Bin Hu at University of Tennessee**)
- 2. "Magnetoconductance responses in conjugated molecules of charge transfer polaron pairs"** in preparation (2011). **(AOARD-10-4054)** (**Joint research work with Prof. Bin Hu at University of Tennessee**)
- 3. "An ambipolar to n-type transformation in pentacene-based organic field-effect transistors"** *Org. Electron.* **12**, 509 (2011). **(AOARD-10-4054)**
- 4. "The extra-high efficiency polymer light-emitting diodes via the formation of layered structure of tetraoctylammonium bromide"** under review **(AOARD-10-4054)**
- 5. "Poly(ethylene oxide)-functionalized Al cathodes of tunable electron-injection capabilities barrier for efficient polymer light-emitting diodes"** in preparation (2011). **(AOARD-10-4054)**

## **IV. Magneto conductance responses in post-annealed polymer photovoltaics**

### **Abstract**

This article studies the variations of magneto conductance (MC) responses in the post-annealed regioregular poly(3-hexylthiophene) (P3HT)-based polymer photovoltaic devices. The short-circuit current ( $I_{sc}$ , photocurrent measured at 0V bias voltage) for P3HT-based photovoltaic of Al electrode (P3HT/Al-device) without the post-annealing process has a positive MC response in  $I_{sc}$  of ~5.0% at B=1000mT. However, upon post-annealed at 150°C for few minutes (5~90 minutes), the maximal magnitudes of MC responses were decreased with the post annealing time. The decreases in MC responses are correlated with the elevated open-circuit voltage for P3HT/Al-devices by the thermal annealing process. The increased built-in electrical field presumably facilitates the dissociation of photo-excited states, but reduces the influence from the applied magnetic field and declines the MC response. A negative MC component, resulting in the gradually decreased MC responses in the high magnetic field (>300 mT), were also observed in  $I_{sc}$  of the post-annealed P3HT/Al-devices at 150°C for 90 minutes due to the reduced triplet exciton-charge reactions.

Keywords: magneto conductance, post-annealed, photovoltaics, P3HT, MC

## 1. Introduction

The electronic devices incorporating organic conjugated molecules/polymers as the active layers, exhibit strong magneto responses. [1, 2] The output performance, such as the electroluminescence, [1, 3-5] resistance or conductance, [1-7] in organic/polymer diodes can be modulated by the applied magnetic field. While the organic/polymer diodes are operated at photovoltaic (PV) regime with illumination, the magnitude of photocurrent is varied with the applied magnetic field. [2, 8-11] Since the photocurrent of P3HT-based diodes is the sum of “current flows” generated by the photo-excited states (excitons and polaron-pair (PP) states), any variations induced by an applied magnetic field on the distribution, dissociation, and charge reaction processes of the singlet/triplet excited states (excitons and PP states) would certainly modulate the magnitude of photocurrent and magneto conductance (MC) response in PV devices. [9, 12] Kalinowski *et al.* reported the dissociation rate of the singlet PP states is higher due to the stronger ionic feature than that of triplet PP states, [10, 13, 14] which is accountable for an increase of free charge carriers and a positive MC effect. In another way, the decline of triplet excitation-charge reactions to charge carriers (reduce in mobility and concentration of triplet excitons), caused by the applied magnetic field, [15-17] results in the decrease of free charge carriers and contributes to a negative MC effect. Xu *et al.* reported the net MC responses of the photovoltaic cells are the sum of positive and negative MC effects. [12, 18] Our previous studies had reported that the MC responses of PVs are modulated by built-in electrical field, which is changed by varying the bias voltages, inserting the dipole layer, and the work function of electrodes. [11, 18] An inversion in MC response is observed at the electrical bias near the open-circuit voltage ( $V_{oc}$ ).

It was reported that the power conversion efficiencies (PCE) of polymer bulk-heterojunction (BHJ) solar cells are markedly enhanced when the morphologies of BHJ polymer films can be carefully controlled through the slow film-casting conditions. [19] Alternatively, the performance of PVs can further be increased by the post-annealing conditions at elevated temperatures, probably due to the improved contact interface in the polymer/electrode junctions and the morphologies of BHJ films. [20] The improvement in the polymer morphologies or the metal/polymer interface can be studied by measuring the MC responses of the devices, [21] because the applied magnetic field can fine tune

the distribution and charge reactions of the excited states, resulting in the magnetic-field-sensitive responses in the photocurrent. [2, 18] Accordingly, the influence of post-annealing conditions on MC responses of polymer PVs was reported in this manuscript. The short-circuit current ( $I_{sc}$ , photocurrent measured at 0V bias voltage) of the device before and after post-annealed at 150°C for few minutes (5~90 minutes) has the distinct MC response, which is correlated with the elevated  $V_{oc}$  by the thermal annealing process for poly(3-hexylthiophene) (P3HT)-based PVs of Al electrode. A decrease in the maximal positive MC response of  $I_{sc}$  and a negative MC component in the high magnetic field (>300 mT) were observed for the post-annealed P3HT/Al-devices at prolonged time.

## 2. Experimental

The polymer diodes and photovoltaic devices are fabricated in a standard arrangement by sandwiching the active layer between a transparent electrode and a metal electrode. The transparent electrode is comprised of the cleaned indium-tin-oxide (ITO) covered glass substrate (RITEK Corp., 15 Ω/□) coated with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Baytron P, Bayer AG, Germany) layer. Regioregular organic P3HT (98.5% electronic grade, Rieke Metals, Inc., USA) is dissolved in chlorobenzene to yield the P3HT (10 mg/ml) solution. The active layers are obtained by spin-coating (700 r.p.m.) the solutions on the PEDOT:PSS/ITO/glass substrates. Al (100 nm) or Ca (40 nm) with Al (100 nm), as metal electrodes, are thermally deposited onto the surface of the active layer inside a vacuum chamber ( $4.0 \times 10^{-6}$  hPa).

A halogen lamp is used as the light source ( $80 \text{ mW/cm}^2$ ) to investigate the MC response of the photovoltaic cells in this study. The devices are encapsulated by the UV-curable epoxy with a cover glass and placed at the direction parallel to the magnetic field. In order to eliminate the influence due to drifting with different bias voltages, the MC curves are averaged, based on the approach reported by Desai *et al.* [4]. The MC magnitude presented in this manuscript is defined as;

$$MC = \frac{\Delta I(B)}{I(0)} = \frac{I(B) - I(0)}{I(0)} \quad (1)$$

Where  $I(B)$  and  $I(0)$  are the current intensity of the photovoltaic cells with and without the applied magnetic field, respectively. All the measurements are performed at room temperature. The magneto conductance of polymer diodes in our study is found to be independent of external magnetic field's direction. [11] The schematic drawings of the device configuration, the measurement of MC responses for polymer diodes under the applied magnetic field with illumination, and the chemical structures of P3HT in this study are illustrated in Figure 1.

### 3. Result and Discussion

#### 3.1 The MC response of P3HT/Al-device

Figure 2 presents the measured MC responses in  $I_{sc}$  for devices with the configurations of ITO/PEDOT:PSS/P3HT/Al (P3HT/Al-device) under the varied post-annealing conditions. The MC response for P3HT/Al-device without the post-annealing process sharply and positively increases with the applied magnetic field (0~300mT), but reaches a saturated level of ~5.0% at the applied magnetic field higher than 500mT. The increased MC response of  $I_{sc}$  in the low applied magnetic field (0~300mT) can be attributed to the increased distribution of singlet PP states, which have a relatively higher dissociation rate for converting into free charge carriers than that of triplet PP states. [10, 13, 14] The schematic mechanisms presenting the generation of positive MC response are illustrated in Figure 3.

As shown in Figure 3, the photo-induced excitons ( $S^1$ ) may undergo a relaxation process to become the excited polaron-pairs (**PP**) states with a longer range of e-h separation distance than that of excitons. Both the excitons and PP states are the excited states of conjugated organic molecules possessing singlet and triplet electronic configurations. Since the magnitude of exchange energy for the singlet/triplet excited states is exponentially decayed with respect to the e-h separation distance. [22, 23] the status of the long-range ( $>1$  nm) PP states having exchange energies of the order smaller than  $10^{-3}$  meV is subjected to changes brought in by the applied magnetic field. [24] The population of singlet and triplet PP states therefore can be modified by the external magnetic field, if the change of the external Zeeman splitting is greater than the internal Zeeman splitting.[24, 25] Kalinowski *et al.* reported the singlet excited states have the

higher dissociation rate to charge carriers than that of triplet PP states due to the fact that singlet PP states have a stronger ionic character than triplets and are stronger coupled with the ionic reaction products of separated holes and electrons. [10] Accordingly, the increased distribution of singlet PP states by the applied magnetic field raises the  $I_{sc}$  (singlet PP states have a relatively higher dissociation rate for converting into free charge carriers than that of triplet PP states), [10, 26] and contributes to a positive and sharply elevated MC response in the low magnetic field (0~300mT) for P3HT/Al-device. However, the distribution of singlet PP states reaches the maximum at the applied magnetic field larger than 500mT, resulting in the saturated MC response of ~5.0% (>500mT) as illustrated in Fig. 2.

### 3.2 The influence of post-annealing processes on MC responses of P3HT/Al-devices

The MC responses for P3HT/Al-devices were markedly changed with the post-annealing conditions (at 150°C for few minutes (5~90 minutes)) as shown in Fig. 2. Firstly, the maximal MC responses were declined from ~5.0% to ~2.5% as the post-annealing time was increased. Secondly, a negative MC component was observed at the applied magnetic field larger than 300 mT, contributing to the gradual decrease of MC responses, as indicated by the dash line in Fig. 2, in the high magnetic field for P3HT/Al-device post-annealed at prolonged time (>30 minutes). It was reported that the PCE of post-annealed P3HT:[6,6]-phenyl C61-butyric acid methyl ester (PCBM)-based polymer bulk-heterojunction solar cells with Al electrode can be largely enhanced to some extent by the essential improvement of the P3HT:PCBM/Al contact interface and the morphologies of P3HT:PCBM films. [20] The photovoltaic measurements, as shown in Fig. 4, indicated that  $V_{oc}$  of the P3HT/Al-devices is elevated with the post-annealing time, which is approximately ~0.27, 0.35, 0.40, and 0.44V for the device without post-annealing process, post-annealed at 150°C for 5, 30, and 90 minutes, respectively. Accordingly, the elevated magnitude of  $V_{oc}$  suggests the increase of the built-in electrical field (potential) of P3HT/Al-device by the post-annealing process, which presumably facilitates the dissociations of photo-induced excited states. However, the enhanced dissociations reduce the influence of the applied magnetic field on the excited states and

result in the decrease of the maximal MC responses (from ~5.0% to ~2.5%) for post-annealed P3HT/Al-devicces as illustrated in Fig. 2.

The gradually decreased MC responses for post-annealed P3HT/Al-device (30 and 90 minutes) at the applied magnetic field higher than 300 mT, as shown in Fig. 2, can be attributed to the negative MC component (-MC) as illustrated in Fig. 3. The densities of triplet exciton of P3HT under illumination are about 77% as reported by Burrows *et al.* [27] for the study of S1~>T1 intersystem crossing in pi-conjugated organic polymers, although the initial excited states in P3HT by photo illumination are singlet based on the selection rule. The triplet excitons can react with free charge carriers in organic materials or metal electrode to dissociate the electron-hole pairs. [16, 28] The exciton-charge reaction is essentially Coulombic interaction between an excited state and a trapped, or free charge carrier, or the metal electrode. [29, 30] However, a magnetic field can decrease the reaction-rate constant by removing the triplet degeneracy or deducing the triplet mobility due to the external Zeeman splitting. [21, 31-33] Although the exciton-charge reactions of both singlet and triplet excitons can contribute the device current, the influence of the applied magnetic field on the exciton-charge reaction of the triplet excitons is more apparent, because of their longer diffusion length and sufficient contacts with charge carriers than those singlet excitons. The triplet exciton-charge reactions are therefore decreased with magnetic field and yield a negative component in MC effect. As the applied magnetic field is further increased, the decrease of triplet exciton-charge reactions causes a simultaneous reduction in the  $I_{sc}$  and accounts for a negative component of MC response. Additionally, the improved P3HT/Al interface of post-annealed P3HT/Al-device enlarges the contact of the excited states in P3HT with Al and fortifies the effect of the applied magnetic field on the triplet exciton-charge reactions with electrode. The other possibility of the negative MC effect on  $I_{sc}$  is a reduction in the initial concentration of triplet excited states. An external magnetic field can increase singlet/triplet population ratio in inter-molecular excited states (PP states) by reducing the intersystem crossing within PP states, [34] that would lead to a decrease in the population of triplet PP states and consequently in the concentration of triplet excitons. Accordingly, the net MC responses for post-annealed P3HT/Al-device (30 and 90 minutes) are the tradeoff between the distribution and dissociation of the singlet PP states (positive MC

component) with the changes on the triplet exciton-charge reactions to charge carriers (negative MC component) under the influence of applied magnetic field as depicted in Fig. 3, which are positively increased in the low magnetic field ( $<\sim 300$  mT) and then gradually decreased as the applied magnetic field is increased ( $>\sim 300$  mT) as shown in Fig. 2.

### 3.3 The influence of built-in electrical field on MC responses of P3HT/Ca-devices

Figure 5 presents the measured MC responses in  $I_{sc}$  for devices with the configurations of ITO/PEDOT:PSS/P3HT/Ca/Al (P3HT/Ca-device) under the varied post-annealing conditions. Unlike the P3HT/Al-devices, MC responses of P3HT/Ca-device before and after post-annealed at 150°C for few minutes (5~90 minutes) are always negative and of the magnitude,  $\sim -3.0\%$ , at  $B=1000$ mT. Since the interfacial barrier height at the polymer/metal junction is reduced by the low work function Ca electrode, P3HT/Ca-device has a better polymer/metal interface for collection of charge carriers than that of P3HT/Al-device, as applied for photovoltaic cells [35, 36]. Alternatively, the high built-in electrical field (potential) of P3HT/Ca-device would accelerate the dissociation of the polaron-pair states in P3HT layer without the magnetic field. (The magnitudes of  $V_{oc}$  are  $\sim 0.27$ V and  $\sim 0.85$ V for P3HT/Al-device and P3HT/Ca-device without the post-annealing process, respectively.) Most of the polaron-pair states probably are dissociated due to the higher built-in electrical field in P3HT/Ca-device. Accordingly, the exciton-charge reactions of triplet excitons would be the dominated mechanism. The charge reaction of triplet excitons are reduced as the applied magnetic field is increased, which decreases the overall photocurrent and hence results in net negative MC responses. In Fig. 5, the post-annealing processes for P3HT/Ca-devices at 150°C from 5~90 minutes only causes a small variation in the magnitude of MC responses, in which the results suggest the improvement of the metal/polymer interface or polymer morphology due to the post-annealing processes has the minor influence on the internal electrical field (built-in potential of P3HT/Ca-device) to the dissociation of polaron-pair states. The MC of P3HT/Ca-device is of  $\sim -3.0\%$  in an applied magnetic field of  $B=1000$ mT.

#### 4. Conclusions

In conclusion, the mechanisms to interpret the MC responses of  $I_{sc}$  for post-annealed P3HT-based photovoltaic devices are correlated with the influence of the applied magnetic field and the internal electrical field (built-in potential) on the photo-excited states (excitons and PP states) of conjugated molecules. The P3HT/Al-device without the post-annealing process has a positive MC response of ~5.0% at B=1000mT. However, upon post-annealed at 150°C for 90 minutes, the maximal magnitudes of MC responses of P3HT/Al-device was markedly decreased (from ~5.0% to ~2.5%) in the low magnetic field (<300 mT) and then gradually decreased as the applied magnetic field is increased (>300mT). Our results have indicated that the elevated  $V_{oc}$  of the P3HT/Al-devices (changes in the built-in electrical field) and improved P3HT/Al contact interface by the post-annealing processes modulate the overall MC response. The studies of MC responses could be used as an alternative approach to investigate the photo-induced excited states for the generation of charge carriers in PV cells.

## Reference

1. Ö. Mermer, G. Veeraraghavan, T. L. Francis, Y. Sheng, D. T. Nguyen, M. Wohlgemann, A. Köhler, M. K. Al-Suti, M. S. Khan, Phys. Rev. B 72 (2005) 205202.
2. P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, Phys. Rev. B 76 (2007) 235202.
3. J. Kalinowski, M. Cocchi, D. Virgili, V. Fattori, P. Di Marco, Phys. Rev. B 70 (2004) 205303.
4. P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, N. A. Morley, M. R. Gibbs, Phys. Rev. B 75 (2007) 094423.
5. F. J. Wang, H. Bässler, Z. V. Vardeny, Phys. Rev. Lett. 101 (2008) 236805.
6. J. D. Bergeson, V. N. Prigodin, D. M. Lincoln, A. J. Epstein, Phys. Rev. Lett. 100 (2008) 067201.
7. F. L. Bloom, W. Wagemans, M. Kemerink, B. Koopmans, Phys. Rev. Lett. 99 (2007) 257201.
8. E. Frankevich, A. Zakhidov, K. Yoshino, Y. Maruyama, K. Yakushi, Phys. Rev. B 53 (1996) 4498.
9. Z. Xu, B. Hu, J. Howe, J. Appl. Phys. 103 (2008) 043909.
10. J. Kalinowski, J. Szmytkowski, W. Stampor, Chem. Phys. Lett. 378 (2003) 380.
11. T. H. Lee, T. F. Guo, J. C. A. Huang, T. C. Wen, Appl. Phys. Lett. 92 (2008) 153303.
12. Z. Xu, B. Hu, Adv. Funct. Mater. 18 (2008) 2611.
13. M. Wohlgemann, Z. V. Vardeny, J. Phys.:Condens. Matter 15 (2003) R83.
14. K. Tandon, S. Ramasesha, S. Mazumdar, Phys. Rev. B 67 (2003) 045109.
15. J. Levinson, S. Z. Weisz, A. Cobas, A. Rolon, J. Chem. Phys. 52 (1970) 2794.
16. W. Helfrich, Phys. Rev. Lett. 16 (1966) 401.
17. H. Killestreiter, H. Baessler, Chem. Phys. Lett. 11 (1971) 411.
18. T. H. Lee, B. Hu, C. L. Tsai, R. S. Guan, T. C. Wen, T. F. Guo, J. C. A. Huang, Org. Electron. 11 (2010) 677.
19. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Nature Mater. 4 (2005) 864.
20. W. Ma, C. Y. Yang, X. Gong, K. H. Lee, A. J. Heeger, Adv. Funct. Mater. 15 (2005) 1617.
21. B. Hu, Y. Wu, Nature Mater. 6 (2007) 985.

22. A. Kadaшchuk, A. Vakhnin, I. Blonski, D. Beljonne, Z. Shuai, J. L. Br  das, V. I. Arkhipov, P. Heremans, E. V. Emelianova, H. B  ssler, Phys. Rev. Lett. 93 (2004) 066803-1.
23. G. D. Scholes, G. Rumbles, Nature Mater. 5 (2006) 683.
24. B. Hu, L. Yan, M. Shao, Adv. Mater. 21 (2009) 1500.
25. Y. Wu, Z. Xu, B. Hu, J. Howe, Phys. Rev. B 75 (2007) 035214.
26. E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman, H. H. H  rhold, Phys. Rev. B 46 (1992) 9320.
27. H. D. Burrows, J. S. de Melo, C. Serpa, L. G. Arnaut, A. P. Monkman, I. Hamblett, S. Navaratnam, J. Chem. Phys. 115 (2001) 9601.
28. M. Wittmer, I. Zschokke-Gr  nacher, J. Chem. Phys. 63 (1975) 4187.
29. H. Bouchriha, G. Delacote, P. Delannoy, M. Schott, J. Physique 35 (1974) 577.
30. J. Kalinowski, Organic light emitting diodes: Principles, Characteristics, and Processes, M. Dekker, New York, 2000, P.107-114.
31. U. E. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.
32. V. Ern, R. E. Merrifield, Phys. Rev. Lett. 21 (1968) 609.
33. I. V. Tolstov, A. V. Belov, M. G. Kaplunov, I. K. Yakuschenko, N. G. Spitsina, M. M. Triebel, E. L. Frankevich, J. Lumin. 112 (2005) 368.
34. J. Kalinowski, M. Cocchi, D. Virgili, P. D. Marco, V. Fattori, Chem. Phys. Lett. 380 (2003) 710.
35. V. D. Mihailetti, P. W. M. Blom, J. C. Hummelen, M. T. Rispens, J. Appl. Phys. 94 (2003) 6849.
36. C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, J. C. Hummelen, Adv. Funct. Mater. 11 (2001) 374.

## Figure captions

FIG. 1. A schematic drawing that illustrates the device configuration, the measurement of MC responses for the polymer PV device under the applied magnetic field with illumination, and the chemical structures of P3HT. SMU represents the source measurement unit.

FIG. 2. MC responses in  $I_{sc}$  for P3HT/Al-device (○) before and (□) after post-annealed at 150 °C for 5 minutes, (◇) 30 minutes, and (△) 90 minutes. The dash lines added in the curves of post-annealed P3HT/Al-device for 30 and 90 minutes indicated the gradual decrease of MC responses at the high magnetic field (>300mT).

FIG. 3. A schematic diagram illustrated the positive (+MC) and negative (-MC) components of MC responses. The net MC response of  $I_{sc}$  is the tradeoff between the distribution and dissociation of the singlet PP states (positive MC component) with the changes on the triplet exciton-charge reactions to charge carriers (negative MC component) under the influence of applied magnetic field. ISC represents the intersystem crossing process of excitons. ISP(B) represents the intersystem crossing process (magnetic-field-sensitive) of PP states.

FIG. 4. The photovoltaic measurements of P3HT/Al-device (○) before and (□) after post-annealed at 150 °C for 5 minutes, (◇) 30 minutes, and (△) 90 minutes.

FIG. 5. MC responses in  $I_{sc}$  for P3HT/Ca-device (○) before and (□) after post-annealed at 150 °C for 5 minutes, (◇) 30 minutes, and (△) 90 minutes.

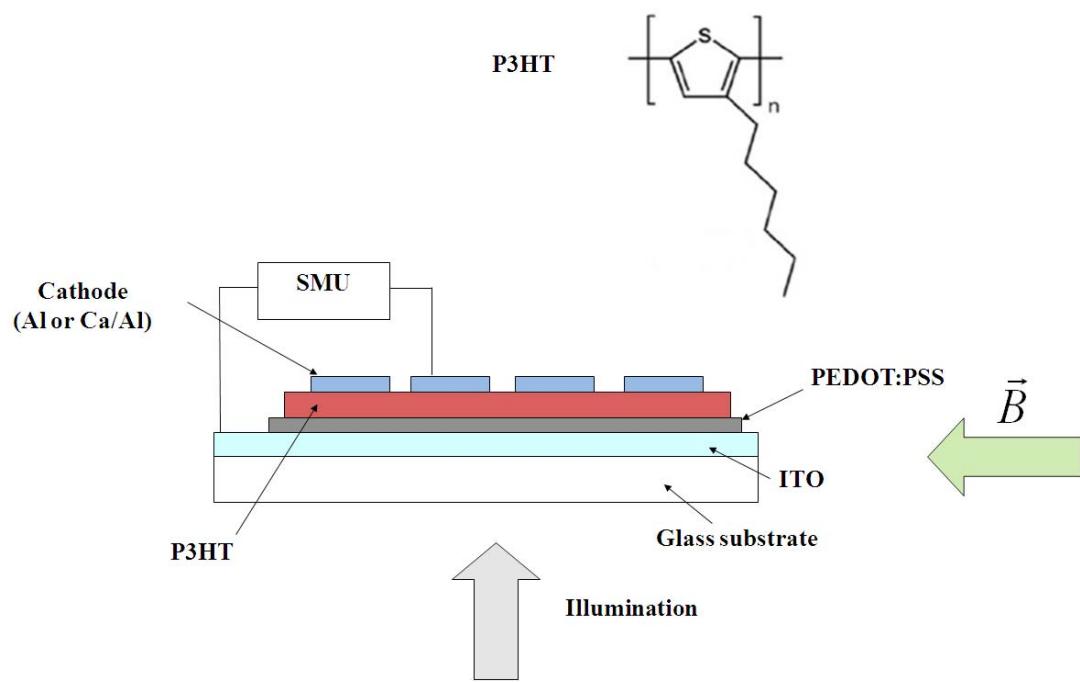


Figure 1

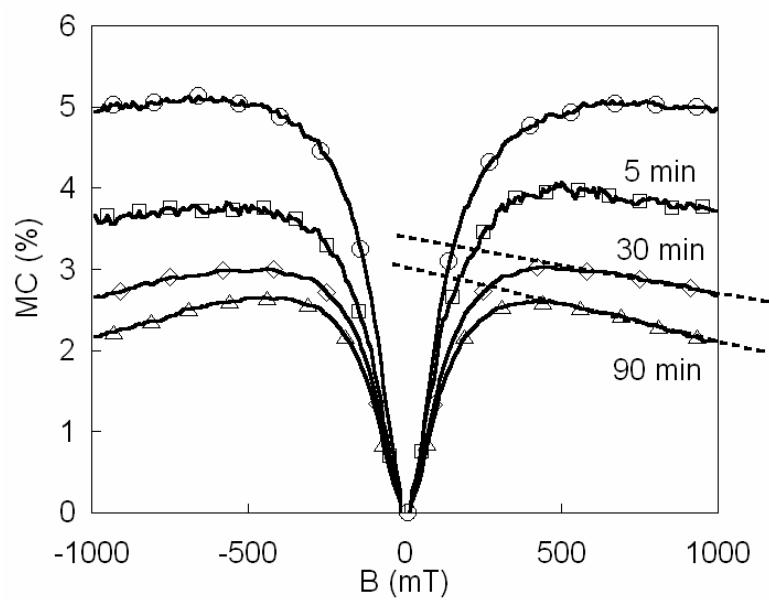


Figure 2

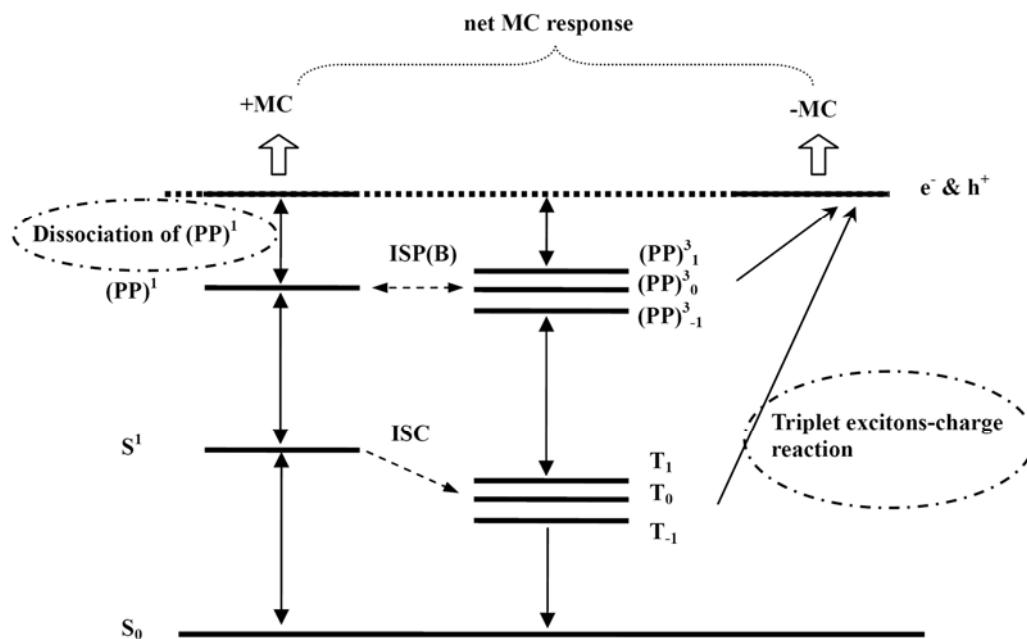


Figure 3

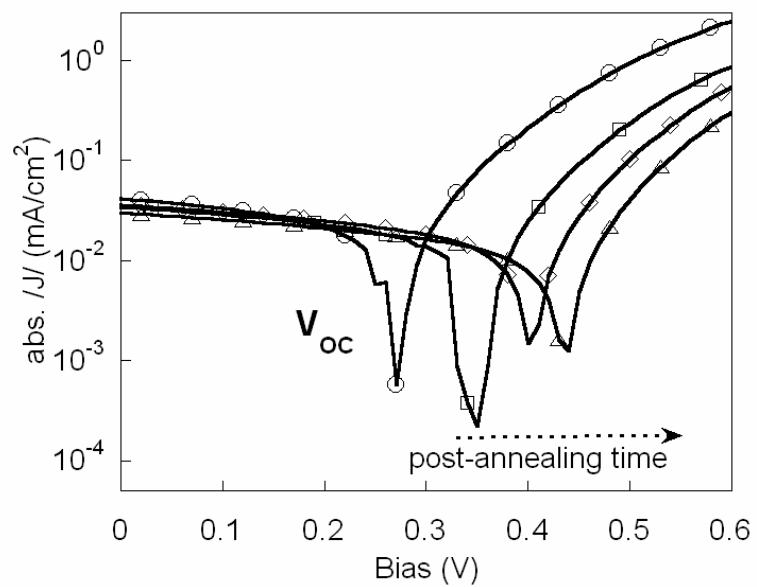


Figure 4

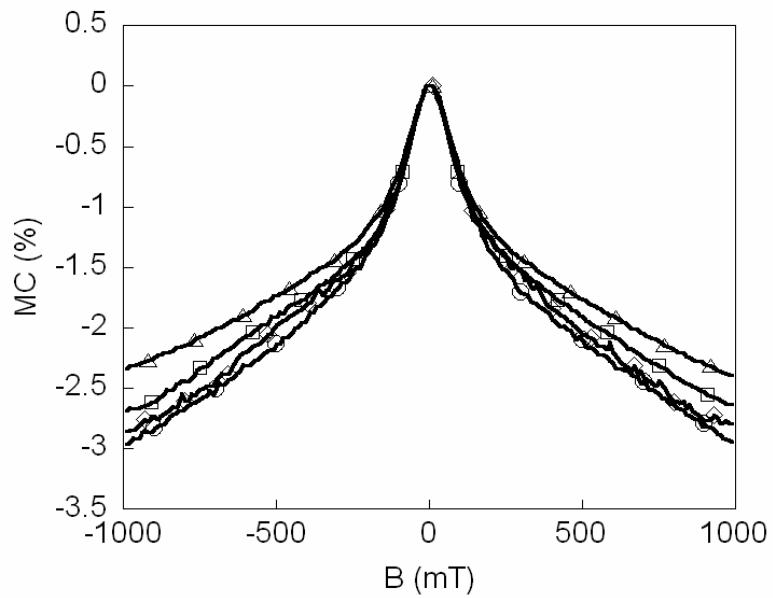


Figure 5

## **VI. Conclusions and Future work**

We had developed a novel cathode design of tunable work functions for the fabrication of high-performance PLEDs and BHJ solar cells. Our research disclosed the origins of the organic molecules/Al junction and further utilize the interfacial reactions to balance the charge carriers and achieve the optimal device performance. PVs applying poly(ethylene oxide)-functionalized Al cathodes have the superior performance than that of devices with low work function metal cathodes. The salt-free, neutral interfacial buffer can be easily integrated with the studies of other types of organic electronic devices, currently in progress. In addition, we recently had extended the our studies to the interface at organic/metal junction for organic field-effect transistors (OFETs). An ambipolar to n-type transformation in pentacene-based organic field-effect transistors (OFETs) of Al source-drain electrodes had been observed in our recent work. The hole currents of the ambipolar OFETs were decreased by over two orders of magnitude within 24 hours after the device fabrication, but the electron currents remained unchanged, which makes the devices present n-type only characteristics. The transformation is correlated with the interfacial interactions between Al electrodes and pentacene, as characterized by analyzing Near-edge X-ray absorption fine structure spectra and Micro-Raman spectra. This study highlights the importance of metal/organic interfaces in the performance of OFETs, and demonstrates decent n-type pentacene-based OFETs.

The charge-transfer complexes would be the critical states to influence the overall power conversion efficiency of BHJ solar cells. The MC responses of charge transfer complexes in poly(3-hexylthiophene) (P3HT):[6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM) BHJ conjugated system was studied in our research. [Lee et al., Org. Electron. 2010, 11, 677] (A joint research work with Prof. Bin Hu at University of Tennessee.) The dissociations of the intermolecular charge-transfer complexes are interfered by the strong Coulmbic interactions in donor-acceptor molecules, which can be characterized by measuring the unique MC responses at the elevated magnetic field. Additionally, MC responses of ground state, charge-transfer complexes are investigated by the conjugated system of N,N'-bis-(1-naphyl)-N,N'-diphenyl-1,1'-biphenyl'-4,4'-diamine (NPB) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). A negative MC response (-0.6%) is observed for NPB:F4-TCNQ(30%) device and is a marked contrast to the negligible MC responses (<0.01%) for devices made of pristine NPB or F4-TCNQ. The MC responses are attributed to the magnetic-field-dependent transport of the injected charge carriers through the localized, charge-transfer complex states in doped NPB:F4-TCNQ system.

We recently had extended the studies of polymer BHJ optically-induced dielectrophoretic (ODEP) devices on the flexible substrates. The bending of flexible substrate causes the marked enhancement of the local electrical field and therefore enlarges the induced ODEP force to drag the microparticles. We had successfully demonstrated the manipulation of polystyrene (PS) beads by flexible polymer ODEP devices with the assistance of deformed substrate, enabling the more efficient separation of PS beads of varied sizes in diameter. Those parts of data will be summarized and submitted soon.

We first report that the self-assembly, well-organized tetraoctylammonium bromide (TOAB) molecules can be nucleated on the surface of active layer to create a lamellar structure by a simple solution process. This superior performance is due to the formation of the molecular dipole from  $\text{Br}^-$  to  $\text{N}^+$  on the surface of active layer. When the direction of the molecular dipole between  $\text{N}^+$  and  $\text{Br}^-$  is reversed on the hydrophilic surface, TOAB can be also used for the fabrication of the inverted device. These results provide a wide thinking: for instance, when the relative position between the anion and cation can be adjusted by different way (eg. the substrate property, the different kind of anion/cation), the dipole direction can be effectively controlled to reduce the electrons/holes injection barriers in PLEDs. This concept is even potentially applied to other organic electronics devices.